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The two- and three-body quenching of XeCl(B,C) by Xe and by mixtures of Xe with He, Ne, Ar and Kr have been measured at 300K. Three-body quenching leads to XeCl* formation. The relaxation processes of the six Xe(6p) states in Xe, Kr, Ar, Ne and He have been characterized at 300K. Experiments were done to characterize the quenching rate constants and the product states from the reactions of these Xe(6p) states with chlorine and fluorine containing molecules.

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INTRODUCTION

The goals of this research effort were to obtain rate data that would aid in the development of a model to describe the complex kinetic processes that occur in the XeCl^* laser media. In particular, the collisional relaxation and reactive quenching of the $\text{Xe}(6p)$ states were studied and compared to the $\text{Xe}(6s)$ states. Also, the electronic quenching reactions of the $\text{XeCl}(B,C)$ molecules were studied under conditions such that the $\text{XeCl}(B)$ and $\text{XeCl}(C)$ molecules were at equilibrium. The two-photon excitation, by a pulsed laser, of Xe atoms in mixtures of Xe with other reagents or with other rare gases was the method used for the preparation of the three $\text{Xe}(6p)$ states with $J=0$ or 2 . The decay kinetics of these three states, as well as the other three states with $J = 1$ or 3 of the $\text{Xe}(6p)$ manifold were monitored by the $\text{Xe}(6p \rightarrow 6s)$ atomic fluorescence. The two-photon, laser-assisted reaction between Xe and Cl_2 was used to prepare the $\text{XeCl}(B,C)$ molecules in mixtures of other gases, and the quenching kinetics were monitored by the $\text{XeCl}(B-X)$ fluorescence. These experimental methods provided clean sources for the state-to-state characterization of the rate processes involving $\text{Xe}(6p)$ atoms and $\text{XeCl}(B,C)$ molecules at 300K. For pressure above 200 Torr of Xe, the formation of Xe_2Cl^* from $\text{XeCl}(B,C)$ was sufficiently rapid that systematic quenching studies of Xe_2Cl^* could be done. The quenching rate constants of $\text{XeCl}(B,C)$ are compared to Xe_2Cl^* .

This report is presented in three parts. A general summary of the principal aspects of the kinetics for the $\text{Xe}(6p)$ states is presented first. Next a summary of the quenching kinetics for $\text{XeCl}(B,C)$ and Xe_2Cl^* is given. Since the majority of the work has been published, or soon will be published, each summary is augmented by the abstracts of the published work. The last section is a listing of the papers that have been, or soon will be,

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published.

Xe(6p) Kinetics

The quenching rate constant for the Xe(6p) states with chlorine donors are always larger than for the Xe(6s) states. Furthermore, the branching fractions for XeCl(B,C) formation are considerably enhanced, relative to those for the Xe(6s) states. For example, the branching fraction for XeCl* formation from HCl are ≥ 0.5 depending to some extent on the specific Xe(6p) state, whereas the branching fraction is only ~ 0.02 for the reaction of Xe(6s) atoms with HCl. With reagents that can act as oxygen and sulfur donors, moderately strong XeO* and XeS* emission was observed from Xe(6p) reactions, whereas the Xe(6s) states give virtually no XeO* or XeS* product. The best donors are N₂O and SCO for XeO* and XeS*, respectively.

A comprehensive study was made for the total relaxation (quenching) rate constants and the product formation rate constants for each of the six Xe(6p) states in Xe, Kr, Ar, Ne and He buffer. The quenching rate constants generally decrease as the rare gas becomes lighter from $1-2 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ for Xe to $1-10 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ for Ne or He. The relaxation mechanism tends to be mainly, but not exclusively, intramultiplet relaxation to the nearest neighbor Xe* state. Thus, the population cascades stepwise through the excited state Xe* levels. The lowest energy Xe(6p) level, the 2p₁₀ state, readily couples to the highest-energy 6s' level, the 1s₂ state. Thus, heavy body collisions mix the Xe(6p) and Xe(6s') manifold of states. By using the state-to-state rate constants measured in our study, it now is possible to model the energy flow through the Xe(6p) manifold as a consequence of heavy body collisions. Detailed results are given in the papers.

By combining the reactive quenching rate constants for halogen donors, in particular chlorine donors, together with the state-to-state relaxation rate constants in rare gas buffers it should be possible to model the role of the Xe(6p) states in a given laser medium involving Xe. Previous work from our laboratory, supported by a different contract, also provides data for higher energy excited Xe states [Inoue, Ku and Setser; J. Chem. Phys. 81, 5760, (1984)].

This section is concluded by abstracts of papers that describe experimental results and discuss the collisional models in terms of intermolecular potentials.

"Significant Enhancement of XeCl(B,C) and XeF(B,C) Formation Rate Constants in Reactions of Xe(5p⁵6p) Atoms with Halogen Donors", J.K. Ku and D.W. Setser, Appl. Phys. Lett. 48, 689 (1986)

The quenching rate constants for Xe(6p) atoms by several halogens and halogen-containing molecules have been measured and they are substantially larger than for reactions of Xe(6s) metastable atoms. The increase tends to be largest for molecules with small Xe(6s³P₂) quenching rate constants, and the Xe(6p) rate constants for NF₃ are 5-20 times larger than for Xe(³P₂). Moreover, the branching fractions for XeCl(B,C) and XeF(B,C) formation are also larger for Xe(6p) atoms than for Xe(6s³P₂) atoms; the branching fractions for XeCl(B,C) formation for HCl are enhanced by more than an order of magnitude. These findings may have important implications for the operation and modeling of rare gas halide lasers and other gas discharge devices.

"Xenon Oxide and Xenon Sulfide Emission Systems at 234 and 227 nm",

J. Xu, D.W. Setser and J.K. Ku, Chem. Phys. Lett. 132, 427 (1986).

The two-body quenching reactions of Xe(6p) excited-state atoms with N₂O and OCS provide moderately efficient sources for generating the electronically excited (ionic) states of XeO* and XeS*. These ionic states decay radiatively via bound-free transitions to the ground-state potentials with intensity maxima at 234 and 227 nm for XeO* and XeS*, respectively. The quenching kinetics of Xe(6p[1/2]₀ and 6p[3/2]₂) with N₂O, OCS, NO₂, SO₂, O₂ and CO and the formation kinetics of XeO* and XeS* are discussed.

"Collisional Deactivation of Xe(5p⁵6p) states in Xe and Ar", J.K. Ku and D.W. Setser, J. Chem. Phys. 84, 4304 (1986).

One-photon excitation in the afterglow of a pulsed discharge and two-photon excitation in a static cell have been used to generate the six Xe(5p⁵6p) states in variable pressures of Xe. The decay times of the initially excited states and their products have been analyzed to obtain state-to-state rate constants at 300 K for collisional transfer among the Xe(5p⁵6p) levels and the Xe(5p⁵6s') levels. The depolarization rate constants for the Xe(5p[5/2]₂) and Xe(5p[3/2]₂) states prepared by two-photon excitation were measured to be $\sim 6 \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹. The collisional deactivation rate constants of the two-photon prepared states, Xe(6p[1/2]₀), Xe(6p[3/2]₂), and Xe(6p[5/2]₂), in Ar also are reported.

"Deactivation Rate Constants and Product Branching in Collisions of the Xe(6p) States with Kr and Ar", J. Xu and D. W. Setser, J. Chem. Phys. In Press (1989).

The quenching kinetics of the Xe(6p[1/2]₀), Xe(6p[3/2]₂) and Xe(6p[5/2]₂) states have been studied in Kr and Ar buffer gas at room temperature using the two-photon, laser-excitation technique. The total quenching rate constants and the primary product distribution were measured to obtain state-to-state rate constants. Collisions between Xe[1/2]₀ and Kr mainly gave energy transfer to Kr(5s, ³P₂) rather than relaxation to the Xe(6p or 5d) levels. The transfer of energy from Kr(5s, ³P₂) back to the Xe(6p) manifold also was observed. The collisional coupling between Xe(6p[1/2]₀) and Xe(3d₅) in Ar, reported previously, was confirmed. The collisions of Kr and Ar with Xe(6p[3/2]₂) and Xe(6p[5/2]₂) atoms gave intramultiplet relaxation; observation of the time dependence of the primary products, the Xe(6p[3/2]₁), (6p[5/2]₃) and (6p[1/2]₁) states, permitted assignment of some state-to-state rate constants for these states. The flow of energy through the Xe(6p) manifold is discussed.

Quenching Rate Constants of XeCl(B,C)

The XeCl(B,C) molecules were generated by the two-photon, laser-assisted reactions between Xe and Cl₂ in ≥20 Torr of Xe in order to ensure vibrational relaxation and equilibration between the XeCl(B) and XeCl(C) electronic states. Thus, all the quenching rate constants are for a true 300K distribution of the XeCl(B,C) populations. The kinetic data are consistent with the recent spectroscopic determination of the 90±2 cm⁻¹

energy separation between XeCl(B) and XeCl(C) , with the latter being the lower energy state. Experiments were done in pure Xe and in Xe/Kr, Xe/Ar and Xe/Ne mixtures for a range of pressure. The data yield the two-body and three-body quenching rate constants at 300K for these rare gases. The experimental data are provided in the paper that has been submitted to J. Chem. Phys. (the abstract is attached as the last part of this section). This work provides the first comprehensive report of the three-body quenching rate constants involving Xe and another rare gas atom, e.g., $\text{XeCl(B,C)} + \text{Ar} + \text{Xe}$. It also was shown that all three-body quenching gives Xe_2Cl^* , there is no "dark" three-body channel.

During the last few weeks of the contract, rate data were collected to obtain two-body quenching rate constants of both XeCl(B,C) and Xe_2Cl^* by reagents, Q, other than rare gases. In these experiments, mixtures of $\text{Cl}_2/\text{Xe}/\text{Q}$ were irradiated with a pulsed dye laser. The decay rates of XeCl(B,C) were monitored vs [Q] for a fixed Xe pressure of 50 Torr. Next the experiments were repeated, but with a Xe pressure of 200 Torr in order to generate Xe_2Cl^* . The decay rate of the Xe_2Cl^* fluorescence was monitored vs [Q] to obtain the quenching rate constants. The reagent molecules include mainly stable diatomic and triatomic molecules plus CF_4 and SF_6 . Since this work is not at a publishable stage, the 300K rate constants are listed in Table 1. The results are somewhat surprising. Although both XeCl^* and Xe_2Cl^* are ionic molecules, the Xe_2Cl^* molecules are quenched much less readily. There appears to be an intrinsic difference in the rate of collisional coupling between the bound XeCl^* states and $\text{Xe}+\text{Cl}$ continuum vs the bound Xe_2Cl^* states and the $2\text{Xe}+\text{Cl}$ continuum. In a practical sense, the generally large quenching rate constants for XeCl(B,C) by small molecules

mean that ultra pure He/Ne and Xe tank gases are essential to achieve high performance for the XeCl(B,C) laser.

Comparison of Two-Body Quenching of XeCl(B,C) and Xe₂Cl* at 300K

Reagent	$k_0 (\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$ Xe ₂ Cl	XeCl
Ar	$<5 \times 10^{-14}$	$(2 \pm 1) \times 10^{-12}$
Kr	$<9 \times 10^{-14}$	$(5.9 \pm 0.3) \times 10^{-12}$
Xe	$<7 \times 10^{-14}$	$(8.0 \pm 2.0) \times 10^{-12}$
N ₂	$(3.9 \pm 0.8) \times 10^{-14}$	$(7.8 \pm 0.2) \times 10^{-12}$
CO	$(8.9 \pm 0.8) \times 10^{-12}$	$(3.7 \pm 0.4) \times 10^{-10}$
O ₂	$(5.1 \pm 0.6) \times 10^{-12}$	$(2.3 \pm 0.2) \times 10^{-10}$
NO	$(2.6 \pm 0.1) \times 10^{-12}$	$(1.1 \pm 0.2) \times 10^{-10}$
HCl	$(6.1 \pm 0.2)^a \times 10^{-10}$	$(6.3 \pm 0.6)^a \times 10^{-10}$
Cl ₂	$(4.0 \pm 0.1) \times 10^{-10}$	$(5.8 \pm 0.6) \times 10^{-10}$
CO ₂	$(3.0 \pm 0.1) \times 10^{-11}$	$(4.9 \pm 0.3) \times 10^{-10}$
N ₂ O	$(9.1 \pm 0.9) \times 10^{-12}$	$(5.3 \pm 0.3) \times 10^{-10}$
CF ₄	$(1.5 \pm 0.4) \times 10^{-13}$	$(5.9 \pm 0.2) \times 10^{-12}$
SF ₆	$(4.0 \pm 0.3) \times 10^{-14}$	$(5.9 \pm 0.6) \times 10^{-12}$

(a) Work from other laboratories

"DECAY KINETICS OF XeCl(B,C) IN Xe AND IN MIXTURES OF Xe WITH Kr, Ar, Ne and He", E. Quiñones, Y. C. Yu, D.W. Setser and G. Lo, J. Chem. Phys. submitted (1989).

The two-photon, laser-assisted reaction between Xe and Cl₂ has been used to prepare XeCl(B,C) molecules in Xe and in mixtures of Xe with lighter rare gases for kinetic studies of the decay of the coupled XeCl(B,C) states. The XeCl(B-X) spectrum was used to assign the conditions for which the vibrational temperature was nearly 300K. Relative intensity and coupled radiative lifetime measurements provide independent data which support an energy separation between the XeCl(B) and XeCl(C) states of $\sim 100 \text{ cm}^{-1}$. The two-body quenching rate constant in Xe for XeCl(B,C) was measured as $8 \pm 2 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$, and a three-body quenching rate constant of $\geq 8 \times 10^{-31} \text{ cm}^6 \text{ s}^{-1}$ is indicated. Experiments also were done with added Kr, Ar, Ne and He, to establish two-body and mixed (e.g., Xe + Ar) three-body quenching rate constants. The three-body quenching rate constants are nearly equal to the Xe₂Cl^{*} formation rate constants and three-body dark quenching of XeCl(B,C) is negligible.

Cumulative Listing of Published Work

1. J. K. Ku and D. W. Setser, "Collisional Deactivation of $\text{Xe}(5p^5 6p)$ States in Xe and Ar", J. Chem. Phys. 84, 4304 (1986).
2. J. K. Ku and D. W. Setser, "Significant Enhancement of $\text{XeCl}(\text{B,C})$ and $\text{XeF}(\text{B,C})$ Formation Rate Constants in Reactions of $\text{Xe}(5p^5 6p)$ Atoms with Halogen Donors", App. Phys. Lett. 48, 689 (1986).
3. J. Xu, D. W. Setser, and J. K. Ku, "Xenon Oxide and Xenon Sulfide Emission Systems at 234 and 227 nm", Chem. Phys. Lett. 132, 427 (1986).
4. J. Xu and D. W. Setser "Collisional Deactivation Studies of $\text{Xe}(6p)$ States in Kr and Ar", J. Chem. Phys. submitted (1989).
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6. J. Xu and D. W. Setser, "Collisional Deactivation Studies of $\text{Xe}(6p)$ States in He and Ne", J. Chem. Phys. To be submitted (1990).
7. Y. C. Yu and D. W. Setser, "Comparison of Quenching Rate Constants for XeCl^* and Xe_2Cl^* ", J. Chem. Phys. to be published.